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ELECTROCHEMICAL METHODS APPLIED TO THE ANALYSIS OF ENVIRONMENTAL SAMPLES

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ABSTRACT

The fundamental principles of electroanalytical methods based on potentiometry, coulometry, conductance, and voltammetry are reviewed, and examples are given of applications to environmental analyses.

The cycling of minerals in the environment involves an aqueous solution at some stage. The ionic nature of dissolved minerals suggests that electrical measurement techniques should be appropriate for their chemical determination. Solutions are electrically neutral over dimensions greater than a few hundred micrometers, however, and measuring ionic species directly is very difficult. The operational problem of observing individual dissolved ionic species has even led a noted electrochemist to announce that he has lost confidence in the theory of ionization (Brenner, 1975).

This brief review summarizes what can be learned about electrolyte solutions from electrical measurements and how these measurements are being applied to the analysis for metallic pollutants. The advantages and limitations of the techniques will be indicated.

To make an electrical measurement, we must convert the ionic process in the solution to an electronic process in the measuring circuit, nearly always through the mediation of an interface between the solution and a metallic conductor, the electrode. The nature of this interface has a profound effect on the properties of the solution

which can be observed. The kinds of measurement are conveniently classified as:

1. The potential difference between two electrodes in the same solution.
2. The current flowing between the electrodes.
3. The impedance of the current path, i.e., the ratio of potential difference to current.

The total quantity of electricity flowing in the external circuit is sometimes of interest because Faraday's law relates it to the extent of chemical reaction taking place at the electrodes. This quantity is usually determined by integrating current over a time interval.

POTENTIOMETRY

Measuring the difference in potential between two points in a solution reduces to measuring the potential between two metallic electrodes that make reversible electrochemical contact with the solution. Reversible contact means that a very small change in the potential applied to the electrodes will make a corresponding change in the direction of the chemical reaction taking place in the cell. Specifically, an H_2 gas electrode and a Ag—AgCl electrode placed in the same solution and connected by an external circuit perform the reaction

$$\tfrac{1}{2}H_{2\,(g)} + AgCl_{(s)} = Ag_{(s)} + HCl\ (\text{solution})$$

If H_2 is supplied at a constant partial pressure, the potential difference of the electrodes, i.e., the electromotive force (emf) of the cell, is a measure of the activity of HCl in solution. This may be a useful analytical result, but it is much more useful to relate the measurement to a single species, e.g., the H^+ ion. We can do this by maintaining the Ag—AgCl electrode at a constant potential by placing it in a solution of fixed chloride concentration (e.g., saturated KCl) which is electrically connected to the test solution by an orifice, salt bridge, or junction that permits only negligible mixing of the solutions. The junction between different solutions, like that between dissimilar metals, is characterized by a potential difference that is a function of composition and temperature. With proper allowance for the junction potential and for the contribution of the reference electrode, the emf of the cell indicates the H^+ activity of the test solution. The correction is made by substituting a standard buffer for the test solution. The pH of the standard is defined to be as consistent as possible with theoretical estimates of the H^+ activity

on the basis of ionic theory; the value does not have strict thermodynamic significance, however.

The familiar glass pH electrode responds almost identically to the hydrogen electrode, but it is much more convenient to use. This device has a useful response over nearly 14 orders of magnitude, with a constant relative error of ~2%. Few, if any, other analytical procedures combine such precision and such a large dynamic range with the desirable features of nondestructive measurement, convenience, and low cost. Nevertheless, the pH electrode has some limitations:

1. A properly functioning reference electrode is as important as the sensing electrode.
2. The pH is defined in terms of thermodynamic activity rather than concentration.
3. Because of the dependence on dilute aqueous standards for calibration, measurement in nonaqueous, partially aqueous, or high-ionic-strength solutions is difficult or ambiguous.
4. The glass membrane shows some response to alkali metal ions in high concentrations.

Table 1 summarizes other types of ion-selective electrodes described in the literature. Nearly all of these are available commercially. Particular glass compositions provide membranes responsive to particular ions, but large excesses of similar ions may interfere to some extent. The dynamic measurement range of each electrode listed in Table 1 is much less than that of the pH electrode, and it is instructive to look into the reason. Salt bridges and pH

TABLE 1

TYPES OF ION-SELECTIVE ELECTRODES COMMERCIALLY AVAILABLE TO ENVIRONMENTAL CHEMISTS

Glass membrane	Solid state		Liquid ion exchange		Gas sensing
Ag^+	Ag^+	I^-	Ba^{2+}	K^+	CO_2
Cu^{2+}	Br^+	Mn^{2+}	BF_4^-	Mg^{2+}	H_2S
Fe^{3+}	Ca^{2+}	Ni^{2+}	Ca^{2+}	NH_4^+	NH_3
H^+	Cd^{2+}	Pb^{2+}	Cl^-	NO_3^-	NO_x
K^+	Cl^-	S^{2-}	ClO_4^-	Pb^{2+}	SO_2
Li^+	CN^-	SCN^-	Cu^{2+}		
Na^+	CO_3^{2-}	SO_4^{2-}			
NH_4^+	Cu^{2+}	Zn^{2+}			
	F^-				

electrodes have been miniaturized to permit measurement of the pH of as little as 1 μl of solution. At pH 11, 1 μl contains about 6×10^6 H^+ ions by calculation. The current sensitivity of good-quality commercial pH meters is about 1 pA; this corresponds to 6×10^6 electronic charges per second. Thus we might expect that an attempt to measure the pH of a 1 μl sample would completely destroy the original character of the specimen. Such is not the case, however, because the solvent water participates in a dissociative equilibrium to provide a large H^+ ion reservoir that maintains the original balance. The OH^- ion, which is determined reciprocally from pH measurements, is, of course, the only other ion with the same relation to solvent water.

Less than 10 years have passed since the first successful ion-selective electrode other than the pH electrode became commercially available. The lanthanum fluoride solid-state sensor for the F^- ion made practicable the fluoridation of drinking water and initiated one of the fastest growing developments in analytical chemistry (*Research/Development*, 1977). The F^- ion-selective electrode responds to about six logarithmic units of concentration of highly ionized fluoride compounds and detects as low as about 0.02 ppm F^-. In the presence of relatively high concentrations of such complexes as ThF_4 and ZrF_4, free F^- can be determined to three orders lower concentrations because of the buffering action of the complexes.

Similarly, the Ag_2S solid-state membrane is very useful for determining Ag^+ or S^{2-} ions. The electrode responds to free Ag^+ or S^{2-} ions down to $10^{-7}M$ when these are the only forms in the solution. In the presence of complexes, however, it gave a theoretical response to free Ag^+ over 24 orders of magnitude (Durst, 1969). This means that for small samples there was an appreciable probability that no Ag^+ ion was present, yet the electrode responded to the thermodynamic activity of Ag^+ in equilibrium with the complex.

Compared with solid-state and glass-membrane electrodes, the liquid-membrane ion-exchange types of electrodes listed in Table 1 generally have much narrower ranges of theoretical response. They do, however, provide sensing capability for different anions.

Specific-ion sensors have been used in ingenious ways for various analyses. Electrodes covered with membranes containing immobilized enzymes detect products of enzymatic reactions. In this way the sensitivity and specificity of enzyme systems have been used to determine such substances as urea, glucose, amino acids, etc (Guilbault and Rohm, 1975). Metal wires coated with ion-exchange materials are inexpensive and provide outstanding selectivity for

many cations (Freiser, 1976). Like other liquid ion-exchange membrane electrodes, their working range extends to 10^{-4} *M* only in favorable cases. By covering a combination sensing and reference electrode with a gas-permeable membrane, we can prepare detectors for dissolved gases. Those for CO_2 and NH_3 are probably the best known and most widely used. A prototype model for H_2S showed anomalous response to dissolved gas concentrations below 0.1 ppm (Hoover, 1975).

COULOMETRY

The quantity of electricity passing through a cell is directly related to the amount of chemical change taking place at reversible electrodes by the Faraday law. As an analytical method, therefore, coulometry is an absolute technique in that it depends on the measurement of amperes and seconds, quite independent of any chemical standards. The precision is outstanding, typically better than 0.1%, but the accuracy is no better than the degree of reversibility of the electrochemical cell. Consequently, great pains must be taken to prevent diffusive mixing of the anode and cathode compartments and to prevent parasitic reactions at the electrodes. Recent developments in coulometry have been well reviewed (Clem, 1973a), and applications have been described recently (Siegerman, Chang, and Thompson, 1975). The technique appears to be most appropriate for the repetitive determination of a major component where the highest precision is required.

CONDUCTANCE

The proportionality constant in Ohm's law is impedance, but electrochemical measurements usually use conductance, which is the reciprocal of the direct-current component of impedance. The specific conductance of a solution, determined for a path length of 1 cm and a uniform cross section of 1 cm^2, is a function of only the concentration and mobility of the charge carriers. Although each ionic species has a characteristic limiting mobility at infinite dilution, the value varies with concentration, and there is no practical way to resolve the contributions of different electrolytes in mixtures. Consequently, specific conductance is a physical property that provides only an approximation of the total ionic concentration of mixtures and has limited analytical use.

Two major applications are in measuring extremely dilute solutions and concentrated solutions of known electrolytes. Specific

conductance is the official and prevalent measure of the salinity of seawater, which has a nearly constant proportion of major ions. In this application conductance is used to estimate density.

Specific conductance has long been used to monitor the purity of distilled or deionized water. In that application a rough estimate of the total ionic impurity may be all that is required, or the impurity may be ascribed to a single species, such as CO_2. Table 2 shows some

TABLE 2

CONCENTRATION OF ELECTROLYTE REQUIRED TO INCREASE SPECIFIC CONDUCTANCE OF WATER TENFOLD

Temp., °C	Water, μS/cm	Sodium chloride, ppm	Hydrochloric acid, ppm	Carbon dioxide, ppm
5	0.016	0.11		
15	0.031	0.16		
25	0.055	0.23	0.05	0.19
35	0.091	0.31		
55	0.142	0.41		

electrolyte concentrations at which the contribution from the ionization of water itself is 10% of the total conductance. In the sub-ppm concentration range, the relation between conductance and concentration can be calculated theoretically more reliably than it can be measured in standard solutions.

Although conductance can be measured by direct-current methods, by use of the reversible electrodes described and of separate current and potential probes, inert metallic electrodes (such as platinum) are more convenient to use. The effect of polarization caused by faradaic electrolysis at the electrodes is reduced by using alternating-current techniques. Useful results can be obtained at power-line frequencies (60 Hz), but frequencies as high as 10 kHz may be needed to reduce polarization of bright platinum in aqueous solution to negligible values (Hoover, 1970).

AMPEROMETRY

The polarization of an electrode in an electrolysis cell can form the basis for a very useful analytical technique by limiting the

faradaic current through the cell. Consider the application of increasingly negative potential to a mercury cathode in an unstirred solution of some easily reducible ion, such as cadmium. At first the distribution of cadmium between ions in solution and atoms in the amalgam will be determined by the half-cell potential of the ion—amalgam couple, and very few ions will be reduced. As the electrode is made more negative, reduction is favored, until essentially every ion that reaches the electrode is reduced. The solution adjacent to the electrode tends to become depleted, and at more negative potentials the faradaic current is limited by the steady-state diffusion of Cd^{2+} to the surface. The steady current then, being diffusion limited, will be directly proportional to the concentration of reducible ion in the bulk solution.

Mercury is a particularly suitable metal for the cathode material in this application because, as a liquid, it can provide an extremely reproducible, clean surface. The high over potential of mercury toward H_2 provides a wide potential range and strong reducing conditions in which to perform analyses without interference from the reduction of H^+ ion or water.

The nature of the counter electrode and of the reaction taking place there is almost immaterial so long as the current through the cell is limited by the reaction at the polarized, or working, electrode. The area of the counter electrode is usually made much larger than that of the polarized electrode to help assure this condition.

In the familiar direct-current polarography, at the dropping mercury electrode the detection limit for most ions is about $1 \times 10^{-5} M$, because the total observed current includes a contribution from capacitative charging of the electrode surface, as well as the desired faradaic current from the electrochemical reduction. The charging current arises from increasing electrode area (as in the growing mercury drop) or from increasing applied potential. Two techniques for improving the analytical sensitivity are described.

Linear sweep voltammetry (LSV) employs a stationary mercury drop electrode and, hence, has constant area and a potential sweep rate of several volts per second. The rapid change in applied potential causes a large charging current but increases the faradaic current even more because the small volume of solution next to the electrode is stripped of reducible ions in a very short time. This technique is best suited to determining a single species since the resolution of more than one reduction wave is poor. The technique is rapid (a single scan takes about 0.1 sec), and it has been partially automated (Afghan, Goulden, and Ryan, 1972). The major limitation to precision in older commercial instruments appears to be the resolution of the

cathode ray tube. Whitnack (1976) described a significant improvement in detection limits by digitizing the current from LSV. The development of modern polarographic instrumentation is discussed by Clem (1973b).

A modern, widely accepted approach to improved sensitivity is differential pulse polarography (DPP). The current is sampled immediately before and near the end of a square voltage pulse superimposed on the ramp potential and synchronized near the end of the mercury drop life. The difference of these signals gives a faradaic current nearly free of charging contributions. The output corresponds to a numerical differentiation of the direct-current polarographic wave and gives well-defined peaks for each reducible species. The voltage ramp rate is typically 2 to 5 mV/sec, and a multi-ion scan may take 5 to 10 min. Detection limits are typically $1 \times 10^{-7} M$ for LSV and $1 \times 10^{-8} M$ for DPP.

Electroactive ions can be preconcentrated very effectively by electrodepositing them at controlled potential on a cathode, preferably a mercury drop or mercury thin film on a substrate such as graphite or glassy carbon. The deposited metals should form only a very dilute amalgam in the mercury. The deposition does not need to be quantitative but should be rigorously controlled so that it can be calibrated by standard additions. The quantity and identity of deposited metals are then determined by quantitatively redissolving the metals into the solution under the control of an anodic voltage scan. This process of anodic stripping voltammetry (ASV) can be conducted with either LSV or DPP current-measuring techniques. The extent of preconcentration depends upon the plating time, which is, conveniently, 2 to 10 min. Detection limits of $1 \times 10^{-10} M$ are readily obtainable. The capabilities and limitations of ASV have been thoroughly reviewed (Copeland and Skogerboe, 1974), and a practical scheme to use multiple cells to shorten the mean analysis time was described by Lowry and Smart (1976). Princeton Applied Research has developed a computerized instrument with capability for all the described polarographic techniques, including automatic sample changing, base-line correction, blank subtraction, and calculation of concentrations from standards run with the samples.

APPLICATIONS

Any analytical method for trace metals has particular characteristics that make it more suitable for some elements or samples than for others. These characteristics complicate the comparison of methods, but, when comparisons must be made, the detection limit

for the total amount of an element (all forms) in the sample is one of the important criteria. When using electrochemical techniques for total elemental determination, the analyst must ensure that all the element is in the form that is detected. This usually involves acidification and often involves removal of organics and objectionable anions. The major advantages and disadvantages of ion-selective electrodes and of ASV are listed in Tables 3 and 4, respectively.

Compared with multielement techniques of atomic emission, atomic absorption, or X-ray fluorescence, the electrochemical methods have an outstanding advantage in cost of instrumentation. The most sophisticated polarographic system is available for less than half the cost of optical or X-ray instruments. On the other hand, the electrochemical techniques suffer severely in respect to the number of elements that can be determined conveniently and sensitively. Cahill and VanLoon (1976) compared atomic absorption spectroscopy and ASV under conditions relevant to environmentalists.

TABLE 3

KNOWN ADVANTAGES AND DISADVANTAGES OF ION-SELECTIVE ELECTRODES FOR ENVIRONMENTAL SAMPLE ANALYSES

Advantages	Disadvantages
Inexpensive ($500–2000)	Respond only to free ionic species
Portable	One ion per electrode
Convenient	Need high ionic strength to calibrate in concentration units
Rapid	High detection limit ($\geq 1 \times 10^{-6} M$)
Uniform relative standard deviation	

TABLE 4

KNOWN ADVANTAGES AND DISADVANTAGES OF ANODIC STRIPPING VOLTAMMETRY FOR ENVIRONMENTAL SAMPLE ANALYSES

Advantages	Disadvantages
Cost ($2,000–25,000)	Slow (5–20 min/analysis)
Sensitivity ($10^{-10} M$)	Limited to metals that form amalgams (principally Cu, Pb, Cd, Zn)
Little pretreatment required	Usually organic compounds must be removed from sample

The strength of electroanalytical methods appears to lie in the loosely defined field of chemical speciation, where they have nearly unique capabilities. The real analytical needs in this area should be determined. Although most "free" ions in aqueous solution (to which ion-selective electrodes respond) are recognized to be hydrated, the environmental significance of the distinction between inner and outer spheres of hydration is not clear, and the definition of an ion pair is still debated. Broad distinctions between stable and labile complexes of ions can be made on the basis of rates of reaction at the polarographic electrode, but few of the ligands in such complexes have been identified.

Chau (1973) measured the copper complexing power of natural and waste waters by titrating with copper and determining the excess polarographically. Values from $1 \times 10^{-7} M$ in Canadian lakes to $2 \times 10^{-6} M$ in sewage effluent, expressed as copper equivalents, were found. The indium complexing power of a raw sewage effluent (Haberman, 1971) and a treated sewage effluent (Hoover, 1973) was similarly estimated as $8 \times 10^{-5} M$ and $3 \times 10^{-5} M$, respectively. Andrew (1976) recently employed the copper ion-selective electrode to distinguish between free and total copper in natural waters and related the concentrations of free copper to toxicity to fish. It should be noted that ASV in samples containing organic compounds is subject to severe distortion because of adsorption on the electrode (Brezonik, Brauner, and Stumm, 1976).

Some of the outstanding needs in applying electrochemical methods to the trace analysis of environmental samples are:

1. More reliable techniques for measuring ionic species under environmental conditions. (Changing the electrolyte between the plating and stripping steps of ASV might alleviate adsorption problems.)

2. Better characterization of the species (especially complexes) that give electrochemical responses.

3. Better sensitivity and selectivity of ion-selective electrodes. [Ion amplification with exchange membranes (Blaedel and Niemann, 1975) is an approach.]

The potential application of electroanalytical chemistry to such problems has barely been tapped.

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